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Structure of Tetrapotassium Dodeca-μ-bromo-hexabromo-*octahedro*-hexaniobate(4−), $K_4[(Nb_6Br_{12})Br_6]$

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Abstract. Formed by heating Nb_3Br_8 and Nb in a KBr/LiBr melt; isotypic with $K_4Nb_6Cl_{18}$. $M_r = 2152\cdot10$, monoclinic, $C2/m$, $a = 10\cdot427\,(1)$, $b = 17\cdot222\,(3)$, $c = 10\cdot996\,(1)$ Å, $\beta = 124\cdot84\,(6)^\circ$, $V = 1620\cdot8\,(5)$ Å^3, $Z = 2$, $D_x = 4\cdot41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 244·72 cm^{-1}, $F(000) = 1904$, room temperature, $R = 0\cdot052$ for 1467 reflections. The crystal structure contains $Nb_6Br_{12}Br_6^{4-}$ anions with d_{Nb-Nb} 2·968 (3) to 2·975 (1) Å, d_{Nb-Br} 2·579 (1) to 2·604 (2) Å (bridging) and 2·755 (2) and 2·812 (2) Å (terminal), respectively.

Introduction. Nb and Ta form halides containing clusters $M_6X_{12}^{n+}$ ($n = 2$, 3, 4) (Schäfer & Schnering, 1964). Niobium iodides are an exception, as only the clusters $Nb_6I_8^{m+}$ ($m = 0$, 2, 3) exist (Bateman, Blount & Dahl, 1966; Simon, von Schnering & Schäfer, 1967; Imoto & Corbett, 1980; Imoto & Simon, 1982; Stollmaier & Simon, 1984). The change of the cluster system is somewhat reflected in the niobium bromide system, where no binary compound with octahedral Nb_6 unit exists but only ternary compounds with $Nb_6Br_{12}^{n+}$ clusters (Fleming, Mueller & McCarley, 1967; Broll, Juza & Schäfer, 1971). In the following the crystal structure of $K_4Nb_6Br_{18}$ is described.

Experimental. The preparation was performed according to Broll, Juza & Schäfer (1971). 0·5 g Nb_3Br_8 (Simon & von Schnering, 1966) and a vacuum-distilled mixture of 2·5 g LiBr/3·5 g KBr were sealed in an Nb tube under argon and kept in an evacuated quartz tube. It was heated at 1063 K for 3 h, slowly cooled (for 4 d) and held at 843 K for 2 d (Simon, 1966). By inclining the furnace the salt was separated from the crystals at 843 K and the ampoule was rapidly quenched.[*] Black crystals sticking to the Nb wall were obtained. D_m not determined. Block-like crystal, 0·1 × 0·15 × 0·25 mm, sealed in a glass capillary under argon. Syntex $P3$ four-circle diffractometer (Mo $K\alpha$ radiation, monochromated by graphite). Lattice parameters refined by least-squares methods from 15 reflections ($19^\circ < \theta < 28^\circ$). ω-scan mode, scan range 1°, variable scan speed between 0·75 and 29·3° min^{-1} (ω). Intensity of the standard reflection 003 varied within ±5·4%. $\sin\theta/\lambda \le 0\cdot65$ Å^{-1}, $-13 \le h \le 11$, $0 \le k \le 21$, $0 \le l \le 14$. 1961 independent reflections measured, 1467 with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for the structure determination. Corrections for Lorentz, polarization and empirical ψ-scan absorption applied. Structure solved by direct methods and refined by blocked-cascade-matrix least squares based on F, $w = 1/\sigma^2(F)$, with the aid of the *SHELXTL* program system (Sheldrick, 1981) on an Eclipse S/250 computer. Final $R = 0\cdot0519$, $wR = 0\cdot0451$, $S = 1\cdot640$ for 70 refined parameters. In final refinement cycle $(\Delta/\sigma)_{max} = 0\cdot003$ for U_{22} of Br(4). Final difference electron density map flat ($+1\cdot88 \ge \Delta\rho \ge -1\cdot26$ e Å^{-3}). Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.[*] An *ORTEP* plot (Johnson, 1965) onto (001) and a plot of the single $[(Nb_6Br_{12})Br_6]^{4-}$ anion are presented in Figs. 1 and 2, respectively. Interatomic distances and bond angles are summarized in Table 2. The compound is isotypic with $K_4[(Nb_6Cl_{12})Cl_6]$ (Simon, von Schnering & Schäfer, 1968).

The $Nb_6Br_{18}^{4-}$ anions form a tetragonally distorted f.c.c. arrangement; all 'tetrahedral voids' are occupied by two K^+ ions, which are 4·610 (4) Å apart. Compared to $K_4Nb_6Cl_{18}$ all distances within the Nb_6Br_{18} unit are elongated as expected. This elongation is especially noticeable with the long distances of the Nb atoms to the terminal atoms $Br^a(5,6)$.[†] Obviously these long distances can be discussed in terms of steric

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[*] Slow cooling to room temperature makes crystals mosaic along [010]. Preparations always led to $K_4Nb_6Br_{18}$. A cluster phase observed earlier (Simon, 1966) could not be reproduced.

[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39902 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[†] X^a (a = *aussen* = outside) refers to terminal ligands, X^i (i = *innen* = inside) to bridging ligands (Schäfer & Schnering, 1964).

0108-2701/85/030308-03$01.50

hindrance between bridging and terminal Br atoms which makes it difficult for the Br^a atom to approach the Nb atom. The nonbonding Br^i—Br^a distances are nearly half an ångström shorter than the calculated van der Waals distance, 3·90 Å (Pauling, 1960). The Nb—Br^a distances [2·755 (2) to 2·812 (2) Å] are comparable to or even slightly longer than the distances with intercluster bridging atoms in Nb_3Br_8, 2·75 Å (Simon & von Schnering, 1966), and in $CsNb_4Br_{11}$, 2·74 Å (Broll, Simon, von Schnering & Schäfer, 1969). Another geometrical detail reveals steric effects due to the size of the Br atom: as usual, all Nb atoms are shifted from the midpoint of the average planes of four surrounding Br^i atoms towards the cluster center. But the extent of this shift is more significant [Nb(1): 0·442 (2), Nb(2): 0·457 (2) Å] in $K_4Nb_6Br_{18}$ than in the case of compounds with $Nb_6Cl_{18}^{n-}$ clusters (Koknat & McCarley, 1974), although the Nb—Nb distances are 0·05 Å longer in the bromide compared to the corresponding chloride.

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (×10^3)

U_{eq} is defined as one third of the trace of the diagonalized $\tilde{U}$ matrix.

	x	y	z	U_{eq}(Å^2)
Nb(1)	2541 (2)	5000	3719 (2)	26 (1)
Nb(2)	50 (1)	862 (1)	6376 (1)	25 (1)
Br(1)	−86 (2)	0	1660 (2)	34 (1)
Br(2)	1974 (1)	3954 (1)	1783 (1)	35 (1)
Br(3)	2076 (1)	3942 (1)	5113 (1)	41 (1)
Br(4)	0	2098 (1)	5000	40 (1)
Br(5)	676 (2)	5000	7948 (2)	49 (1)
Br(6)	−135 (2)	2016 (1)	1772 (1)	47 (1)
K	2206 (4)	3389 (2)	8290 (4)	69 (2)

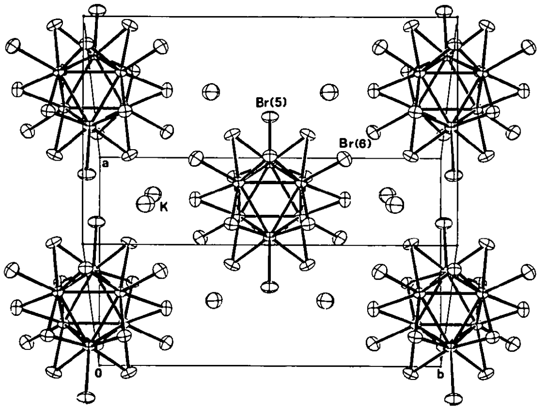

Fig. 1. Projection of the crystal structure on the (001) plane with thermal ellipsoids scaled at the 50% probability level.

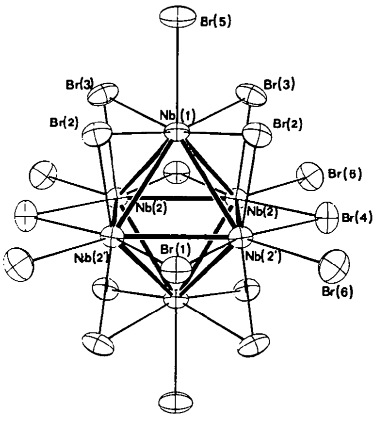

Fig. 2. The structure of the $[(Nb_6Br_{12})Br_6]^{4-}$ cluster anion with thermal ellipsoids at the 50% probability level.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Nb(1)–Nb(2)	2·975 (1)
Nb(1)–Nb(2′)	2·971 (2)
Nb(2)–Nb(2)	2·968 (3)
Nb(1)–Nb(1)	4·211 (3)
Nb(2)–Nb(2′)	4·197 (2)
Nb(1)–Br(2)	2·587 (2)
Nb(1)–Br(3)	2·598 (2)
Nb(2)–Br(1)	2·604 (2)
Nb(2)–Br(2)	2·579 (1)
Nb(2)–Br(3)	2·595 (2)
Nb(2)–Br(4)	2·594 (2)
Nb(1)–Br(5)	2·755 (2)
Nb(2)–Br(6)	2·812 (2)
Br(1)–Br(2)	3·624 (3)
Br(1)–Br(3)	3·611 (2)
Br(2)–Br(2)	3·603 (3)
Br(2)–Br(3)	3·602 (2)
Br(2)–Br(4)	3·605 (1)
Br(3)–Br(3)	3·642 (3)
Br(3)–Br(4)	3·599 (2)
Br(1)–Br(6)	3·476 (2)
Br(2)–Br(5)	3·451 (3)
Br(2)–Br(6)	3·452 (2)
Br(3)–Br(5)	3·442 (2)
Br(3)–Br(6)	3·486 (2)
Br(4)–Br(6)	3·474 (2)
Closest anion–anion contacts	
Br(2)–Br(2)	3·726 (2)
Br(1)–Br(1)	3·755 (5)
Br(3)–Br(4)	3·807 (2)
Br(1)–Br(5)	3·947 (2)
Br(2)–Br(6)	3·992 (2)
Br(2)–Br(5)	4·042 (2)
Br(6)–Br(6)	4·064 (4)
Closest anion–cation contacts	
K–Br(5)	3·114 (1)
K–Br(6)	3·171 (3)
K–Br(6)	3·176 (2)
K–Br(6)	3·272 (2)
K–Br(3)	3·549 (3)
K–Br(4)	3·717 (2)

Nb(1)–Nb(2)–Nb(2)	60·0 (1)
Nb(1)–Nb(2)–Nb(2′)	60·0 (1)
Nb(1)–Nb(2′)–Nb(2)	60·1 (1)
Nb(1)–Nb(2′)–Nb(2′)	60·1 (1)
Nb(2)–Nb(1)–Nb(2)	59·9 (1)
Nb(2)–Nb(1)–Nb(2′)	59·9 (1)
Nb(2′)–Nb(1)–Nb(2′)	59·9 (1)
Nb(1)–Nb(2)–Nb(1)	90·2 (1)
Nb(2)–Nb(1)–Nb(2)	89·8 (1)
Nb(2)–Nb(2)–Nb(2′)	90·0 (0)
Nb(2)–Nb(1)–Br(2)	54·8 (1)
Nb(2)–Nb(1)–Br(3)	55·0 (1)
Nb(1)–Nb(2)–Br(2)	55·0 (1)
Nb(1)–Nb(2)–Br(3)	55·1 (1)
Nb(2)–Nb(2)–Br(1)	55·3 (1)
Nb(2)–Nb(2)–Br(4)	55·1 (1)
Br(2)–Nb(1)–Br(2)	88·3 (1)
Br(2)–Nb(1)–Br(3)	88·0 (1)
Br(2)–Nb(1)–Br(5)	80·4 (1)
Br(3)–Nb(1)–Br(3)	89·0 (1)
Br(3)–Nb(1)–Br(5)	80·0 (1)
Br(1)–Nb(2)–Br(3)	88·0 (1)
Br(1)–Nb(2)–Br(2)	88·7 (1)
Br(1)–Nb(2)–Br(6)	79·8 (1)
Br(2)–Nb(2)–Br(4)	88·4 (1)
Br(2)–Nb(2)–Br(6)	79·5 (1)
Br(3)–Nb(2)–Br(4)	87·8 (1)
Br(3)–Nb(2)–Br(6)	80·2 (1)
Br(4)–Nb(2)–Br(6)	79·9 (1)
Nb(2)–Br(1)–Nb(2)	69·5 (1)
Nb(2)–Br(2)–Nb(1)	70·2 (1)
Nb(2)–Br(3)–Nb(1)	69·9 (1)
Nb(2)–Br(4)–Nb(2)	69·8 (1)
Br(2)–Nb(1)–Br(3)	160·4 (1)
Br(2)–Nb(2)–Br(3)	159·7 (1)
Br(1)–Nb(2)–Br(4)	159·6 (1)

References

Bateman, L. R., Blount, J. F. & Dahl, L. F. (1966). *J. Am. Chem. Soc.* **88**, 1082–1084.

Broll, V. A., Juza, D. & Schäfer, H. (1971). *Z. Anorg. Allg. Chem.* **382**, 69–79.

BROLL, V. A., SIMON, A., VON SCHNERING, H. G. & SCHÄFER, H. (1969). *Z. Anorg. Allg. Chem.* **367**, 1–18.

FLEMING, P. B., MUELLER, L. A. & MCCARLEY, R. E. (1967). *Inorg. Chem.* **6**, 1–4.

IMOTO, H. & CORBETT, J. D. (1980). *Inorg. Chem.* **19**, 1241–1245.

IMOTO, H. & SIMON, A. (1982). *Inorg. Chem.* **21**, 308–319.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KOKNAT, F. W. & MCCARLEY, R. E. (1974). *Inorg. Chem.* **13**, 295–300.

PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca, New York: Cornell Univ. Press.

SCHÄFER, H. & SCHNERING, H. G. (1964). *Angew. Chem.* **76**, 833–849.

SHELDRICK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

SIMON, A. (1966). *Präparative und strukturelle Untersuchungen an niederen Niobhalogeniden mit Me_n-Gruppen.* Doctoral thesis, Univ. of Münster.

SIMON, A. & VON SCHNERING, H. G. (1966). *J. Less-Common Met.* **11**, 31–46.

SIMON, A., VON SCHNERING, H. G. & SCHÄFER, H. (1967). *Z. Anorg. Allg. Chem.* **355**, 295–310.

SIMON, A., VON SCHNERING, H. G. & SCHÄFER, H. (1968). *Z. Anorg. Allg. Chem.* **361**, 235–248.

STOLLMAIER, F. & SIMON, A. (1984). *Inorg. Chem.* In the press.

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$Pr_{15}Ni_7Si_{10}$ with an Atom Ordering on the Trigonal-Prism-Centre Sites in Agreement with the Waist-Contact Restriction Rule

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Abstract. $M_r = 2805{\cdot}44$, hexagonal, $hP64$, $P6_3/m$, $a = 19{\cdot}881\ (1)$, $c = 4{\cdot}2554\ (3)$ Å, $V = 1456{\cdot}7\ (1)$ Å^3, $Z = 2$, $D_x = 6{\cdot}396$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 292$ cm^{-1}, $F(000) = 2442$, room temperature, final $R = 0{\cdot}054$ for 876 contributing reflections. The $Pr_{15}Ni_7Si_{10}$ structure is a member of the structure series $Pr_{n^2+3n+2}Ni_{n^2-n+2}Si_{n^2+n}$ with $n = 4$, characterized by Ni- and Si-centred rare-earth prisms which form trigonal columns, four prisms wide. Where the corners of the trigonal columns meet, a column of face-joined compressed octahedra is formed. The composition of the series and of $Pr_{15}Ni_7Si_{10}$ corresponds to the case where each octahedral void is occupied by one Ni atom. $Pr_{15}Ni_7Si_{10}$ has the same structure sites as the earlier reported $Pr_{15}Ni_4Si_{13}$ ($Ce_{15}Ni_4Si_{13}$ type) but an ordered arrangement of Ni and Si atoms on the prism-centre sites in agreement with the waist-contact restriction rule.

Introduction. In a recent study on the classification of ternary ordered rare-earth (Y, Sc) (*R*)–transition-metal (*T*) silicides and homologues (*M*), built up of centred trigonal rare-earth prisms, some observations have been made concerning the ordering of the *T* and *M* elements on the prism-centre sites (Parthé, Chabot & Hovestreydt, 1983). It was found, that in the case of elongated trigonal prisms (*M*-centred prisms are always elongated, *T*-centred prisms are elongated only if they have a common rectangular face with an *M*-centred prism) the atom ordering obeys the following restriction rule: Neither *R*–*T* nor *T*–*T* waist contacts are allowed. This rule has permitted the interpretation of the atomic ordering in $Pr_{14}Ni_6Si_{11}$ (*mC*124, *C*2/*m*), $Ce_7Ni_2Si_5$ (*oP*56, *Pnma*), Gd_3NiSi_2 (*oP*24, *Pnma*) and LaPtSi (*tI*12, $I4_1md$), for example. The usefulness of this rule for the understanding of the atom ordering of these compounds led us to reinvestigate the structures of other ternary compounds built up of centred trigonal prisms where no or only partial atom ordering was reported and/or where the waist-contact restriction rule apeared to be violated.

The structures of three hexagonal compounds in the system Ce–Ni–Si can be grouped in the form of a structure series with general formula

$$R_{n^2+3n+2}T_2^{[6,o]}\,(T,M)_{2n^2}^{[6,p]}.$$

They are $Ce_6Ni_2Si_3$ (*hP*22, $P6_3/m$) with $n = 2$ (Bodak, Gladyshevskii & Kharchenko, 1974), $Ce_5Ni_2Si_3$ (*hP*40, $P6_3/m$) with $n = 3$ (Bodak, Gladyshevskii & Mys'kiv, 1972)* and $Ce_{15}Ni_4Si_{13}$ (*hP*64, $P6_3/m$) with $n = 4$ (Mys'kiv, Bodak & Gladyshevskii, 1974). These structures are characterized by infinite triangular columns, parallel to [0001], constructed of face-joined, Ni- and Si-centred, trigonal Ce prisms. The parameter *n*

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* In the title of the publication the compound is referred to as Ce_2NiSi.

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